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COLLOID CHEMISTRY AND ITS RELATION TO TANK TREATMENT OF SEWAGE¹

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INTRODUCTION

The importance of colloids in the treatment of sewage has been recognized for many years. Considerable work was done about ten years ago to develop methods of application of principles of colloid chemistry as understood at that time. The results of these efforts were not very encouraging and consequently interest in the study of the colloids of sewage waned for a number of years. Within the last two or three years, improved methods of study have been developed. New processes of treatment, namely, the activated sludge and the Miles acid processes, have had a striking effect upon the colloids of sewage. As a result interest has been reawakened. The purpose of this paper is to summarize the work that has been done, to point out the methods used in the determination of colloids, with suggestions as to their standardization, and to review briefly the results of processes which aimed at the removal of the colloids of sewage.

DEFINITION OF COLLOIDS

From the practical sewage chemist's standpoint, colloids are finely divided solids which will not settle during quiescent sedimentation for many hours. Such a definition is, however, an approximation. From the definitions of actual size of colloidal particles given by Ostwald, Zsigmondy and Hatschek, colloids may range from approximately 0.001 micron to 1 micron in diameter. (A micron is 0.001 millimeter.) The pores of most filter papers are larger than 1 micron. Consequently colloids should pass through filter paper. Such a definition would exclude some suspended matter considered in the

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rough definition previously given. Bacteria are about the same size as colloidal particles, and in many cases larger. Some colloids, as for instance finely divided clay, may stay in suspension for months. Such particles are sometimes smaller than bacteria, and may pass through a rapid filter, when bacteria are removed.

The colloidal state is thus midway between a true solution and suspension. Colloids in sewage are unstable, and may either be going into a true solution or flocculating and precipitating. Sewage colloids usually are of an organic nature, containing nitrogen and sulphur, but inorganic colloids may be introduced by industrial wastes.

IMPORTANCE OF COLLOIDS

Heretofore the sewage chemist has had only a casual interest in colloids, and that largely from the standpoint of measuring the relative degrees of improvement which might be accomplished if all suspended matter could be removed, both in coarse suspension and in a higher degree of dispersion down to solids in true solution.

With the strong interest awakened in activated sludge, the need of a better understanding and perhaps of a method of measurement has arisen. The large surfaces of the particles of activated sludge, and possibly other agencies not fully understood, accomplish almost complete coagulation of colloids. When the sludge is in its best condition it will remove practically all of the colloids from sewage. When under-aerated, apparently not all colloids are removed. When over-aerated the sludge is more finely dispersed and put back in colloidal condition in the effluent. A simple method for the determination of colloids would be of considerable value for the control of an activated sludge plant.

SEPARATION AND DETERMINATION OF COLLOIDS

For the ready classification of colloids, for practical purposes, we suggest that a designated standard grade of filter paper be taken, with pores of such size as to pass particles about 1 micron in diameter. The point of separation between the colloids and crystalloids in this filtrate can hardly be defined, although true crystalloids may be as large as 0.01 micron in diameter.

Various methods have been suggested for the determination of colloids. (a) Graham's method.⁴ This method is based on dial-

⁴ Zsigmondy and Spear, *The Chemistry of Colloids*. 7-8, 1917.

ysis, a process discovered by Graham (1861), who noted the fact that colloids have no marked tendency toward diffusion or passage through parchment membranes. In the simplest form the dialyzer or apparatus may be a cylindrical hard rubber ring, over one end of which a parchment membrane is stretched and fastened. This is set afloat on distilled water in a dish.

The liquid to be dialyzed is placed inside the cylinder. Crystalloids will pass through the parchment into the distilled water, until a condition of equilibrium is reached, when the distilled water must be removed and fresh distilled water added. The colloids remain within the cylinder. By evaporation of the distilled water (which now contains practically all the crystalloids) the weight of crystalloids originally present in the sample may be obtained. This method is not applicable to raw sewage, however, as it requires 12 hours or longer, in which time marked changes in the condition of sewage may be effected by bacteria.

(b) Fowler's method.⁵ Fowler proposes to precipitate the colloids by adding to a 200 cc. portion of the sewage 2 cc. of a 5 per cent solution of sodium acetate and 2 cc. of a 10 per cent solution of ferric ammonium alum. The sample is then boiled for 2 minutes, cooled and filtered. The colloids are precipitated, leaving a clear filtrate, which is supposed to contain only substances in true solution. Fowler states "this method has been found to yield as instructive results as the method of dialysis, while it occupies much less time, and probably in consequence is less liable to error." Fowler determines the oxygen consumed and albuminoid ammonia before and after removal of the colloid, and claims the difference is due to colloids.

(c) Rohland's method.⁶ This method is based upon the adsorption of aniline blue dye by colloids. To a filtered sample of 100 cc. volume, 1 cc. of aniline blue is added, the sample is evaporated to syrup, dissolved in hot water, and filtered. The filtrate is made up to a definite volume, and the blue determined colorimetrically by comparison with known standard concentrations. This has been used by Rohland on sewage, tannery and beet sugar wastes.

(d) Bach's method.⁷ Bach points out that colloids cannot be isolated from sewage, and must be determined by a method which

⁵ Journ. Soc. Chem. Ind., xxvii, 205 (1908).

⁶ P. Rohland, Stuttgart, Z. Anal. Chem. 52, 657-60; Chem. Ab. 7, 4030 (1912).

⁷ The Determination of Colloids in Sewage, H. Bach. Gesundheit Ingenieur, 51, 600-602, Dec. 18, 1920.

bears the same relation to the total content of colloids, that such a method as the permanganate oxygen consumed bears to the total content of organic matter. The optical method proposed by Marc has been modified in the laboratory of the Emschergerossenschaft, to use the determination of the permanganate oxygen consumed. The oxygen consumed by the colloids is found from the difference between that of the colloidal plus dissolved solids and that of the solids in solution. Ignited barium sulphate is used to adsorb the colloids.

(e) Marc's method.⁸ This method uses the interferometer, a costly instrument similar to a refractometer. This is affected by solids in solution as well as in colloidal suspension. Bach states that it has been discarded for his method.

(f) Other methods. The nephelometer may be applicable. In the work of the Sanitary District of Chicago a Kober nephelometer⁹ is to be used.

In view of the wide range of methods that have been used, we believe some attention might be given to the development of a standard method, which would serve to fix more definitely the true importance of the removal of colloids in sewage treatment. Many have assumed that the removal of colloids is the most important factor in reducing the oxygen demand and putrescibility of sewages.

REMOVAL OF COLLOIDS BY TANK TREATMENT

Various analyses cited by Metcalf and Eddy¹⁰ show contents of colloids at Leeds of 30 per cent of the albuminoid ammonia in raw sewage and 42.5 per cent after pumping, 14.9 per cent of the oxygen consumed before and 17.2 per cent after pumping, whereas at Philadelphia 36 per cent of the oxygen consumed was in colloidal form, and 18.5 per cent settled in 2 hours.

Up to the present time, only a few experiments have been made on removing the colloidal matter by tank treatment. As our discussion shows, colloidal matter, strictly defined, will practically pass through and out of a tank with the usual periods from 2 to 4 hours, employed in the settling chambers of Imhoff tanks.

⁸ The Determination of the Concentration of Colloid Solutions by Means of the New Liquid Interferometer. Dr. Marc. Chem. Ztg. 5, 537 (1912).

⁹ Journ. Biol. Chem. 29, 2, 155 (1917).

¹⁰ American Sewerage Practice, Metcalf and Eddy, Vol. III (1st ed.) pp. 168-171.

In the Travis tank¹¹ an attempt has been made to coagulate the colloids on the surfaces of colloidors. These are series of slats hung in the settling chamber, spaced about 3 in. apart transversely and 5 to 9 in. longitudinally.

Chemical precipitation is an effective method of removing colloids. It is generally assumed that the efficiency of this method is due mainly to the coagulating effect of the precipitate formed, calcium carbonate with lime, aluminium hydroxide with alum, or ferric hydroxide with iron sulphate. There may also be an additional adsorptive effect in this type of precipitation, by which the colloids are coagulated on the surfaces of the precipitated flocs.

Another type of chemical precipitation which has not been investigated to any great extent is that in which an acid is used, either sulphuric acid, or, as proposed in the Miles process, sulphurous acid. It is known that certain colloids are electrically charged, positively or negatively. The strength of these charges on sewage colloids is not known accurately, but it is generally assumed that the charge is negative. It is a principle of colloid chemistry that colloids may be coagulated by the addition of substances having an opposite charge, the completeness of coagulation varying, but reaching an optimum at the point where the charge on the colloid is completely neutralized. Therefore in chemical precipitation, it is desirable to add substances which will neutralize these charges, and to add them in such amounts as just to reach the isoelectric point, the point of complete neutralization. If all sewage colloids carry a negative charge, the addition of acids, which carry a positive charge due to hydrogen-ions, should neutralize the negative charges and coagulate the colloids. It was found at New Haven that this did occur upon the addition of sulphurous acid in the Miles acid process, but the removal of colloids was far from complete.

In the experiments on Packingtown Sewage the use of acid made a reduction on the crude sewage in the oxygen requirement of about 40 per cent, as compared with a reduction in the Imhoff tanks settling, between 23 and 32 per cent.¹²

Recent conceptions of the rôle of colloids in sewage treatment lay great stress upon determinations of the concentration of hydrogen-

¹¹ American Sewerage Practice, Metcalf and Eddy, Vol. III (1st ed.) pp. 415-6.

¹² Report on Industrial Wastes from Stockyards and Packingtown, Vol. II (1921), p. 47.

ions or the pH (the logarithm of the reciprocal of the concentration of hydrogen-ions). This method of attack may yield valuable results, but there are more factors involved than simply the condition of acidity or alkalinity. Good judgment must be used in drawing conclusions from the results of pH determinations.

Coagulation of colloids may also be effected by biological agencies. In the activated sludge process there is a possibility that enzymes have a clotting effect. The films in a sprinkling filter may have a biological significance in the removal of colloids, aside from their physical effect of adsorption.

At the Lawrence Experiment Station, Clark¹³ has experimented with colloids, in aeration tanks, with considerable success, "The sewage was aerated in a tank containing slabs of slate about 1 inch

LIQUID	DISSOLVED OXYGEN REQUIRED PER LITER	DISSOLVED OXYGEN INITIALLY PRESENT PER LITER	TRUE RELATIVE STABILITY CALCULATED
	<i>mgm.</i>	<i>mgm.</i>	
Crude sewage.....	96	1.0	1.0
Sedimentation.....	84	1.7	2.0
Septic.....	72	0.2	0.3
Biolytic.....	72	0.1	0.1
Emscher.....	60	1.2	2.0
Filtered crude.....	48	1.0	2.1
Sprinkling filter effluent.....	8	7.6	95.0

apart. After a few hours treatment in the tank the sewage is quite free from both suspended and colloidal matters."

In the work of the Sanitary District, the so-called biolytic tank was of interest, because of the precipitation of the visible colloids. In the tank all the incoming sewage passed upwards and through the accumulation of sludge. While septic action prevailed, with constant generation of hydrogen sulphide, a marked clarification resulted. The action was also marked by the bacterial decomposition of the sulphates in the sewage. The presence of a little iron from a wire mill waste was helpful. In rainy weather, with storm water present, the clarification disappeared. The same general phenomena have been noted in many so-called "successful" septic tanks, which produce clear effluents.

¹³ Report Massachusetts State Board of Health, 1912, pp. 290-2.

In the above mentioned investigations at Chicago, Langdon Pearce and Dr. Arthur Lederer found a considerable improvement over tank effluents, by the removal of all the suspended solids by filtration through filter paper.

The relative rates of exhaustion of the oxygen is indicated approximately in figure 1. The few points available show that the amount of oxygen used up in a given number of hours is appreciably less for filtered sewage than for settled sewage, and less for settled sewage than for crude.

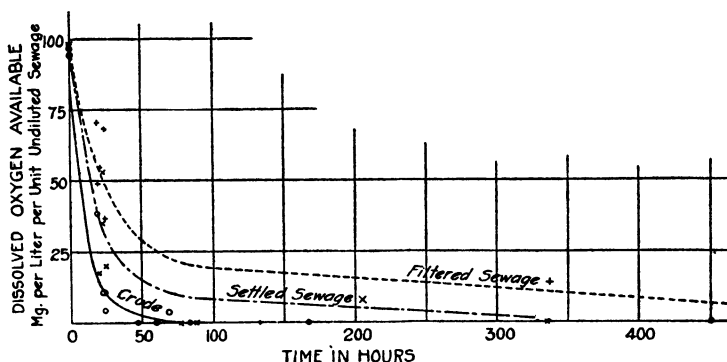


FIG. 1. RELATIVE RATES OF EXHAUSTION OF OXYGEN IN DIFFERENT CONDITIONS OF SEWAGE

DEWATERING SLUDGE

Interesting developments may be hoped for in the application of methods of colloid chemical research to the problems of dewatering sewage sludges. For example, we do not know why fresh sewage sludge is so retentive of its water, while digested sludge parts with it so much more easily. The moisture content of Imhoff sludge varies widely with different sewages, and many problems in its digestion are still unsolved. With activated sludge marked progress has already been made by Wilson and Heisig¹⁴ at Milwaukee.

A wide field lies open before the colloid chemist in the investigation of sewage sludge, but the record of past failures to solve the problem adequately indicates that progress may be slow.

¹⁴ Jour. of Industrial and Engineering Chemistry, Vol. 13, 406-10 (1921).

CONCLUSION

To summarize, it is apparent that we are in need of:

1. A standard definition of the limits of size of colloids in sewage.
2. A standard method for the determination of sewage colloids.
3. The study of the effect of the hydrogen-ion concentration on the removal of colloids, correlated with other determinations and observations which will prove the validity of such pH determination.
4. Tests of the practical application of precipitants which have been found effective in laboratory experiments.
5. Investigation of the principle governing the retention of moisture by sewage sludge.

As yet in the removal of colloids by tank treatment, but little has been accomplished in a practical way, by settling alone, or by the use of coagulants. Chemical precipitation by alkaline precipitants removes some of the colloidal matter, but adds so much to the bulk of the sludge, that the process has not proved popular, and is restricted in its present application to special cases.

The use of acids, instead of alkaline precipitants, yields a well clarified effluent, in many cases without the large bulk of sludge, but has not proved applicable except under special conditions.

Activated sludge is effective in removing colloids, but is not classed as a tank treatment under the scope of this paper.